Supplemental material of ”Cooperation and competition between magnetism and chemisorption”

Satadeep Bhattacharjee and Seung-Cheol Lee

Indo-Korea Science and Technology Center (IKST), Bangalore, India

(Dated: November 19, 2020)

Derivation of the Eq.3 of the manuscript

The adsorption energy is given by,

$$\begin{aligned}
\Delta E(\delta m) &= \sum_{\sigma}\{\int^{E_F+\delta E_F} E\tilde{D}_{\sigma}(E)dE - \int^{E_F} ED_{\sigma}(E)dE - n_{a\sigma}\varepsilon_{a\sigma}\} \\
&= \sum_{\sigma}\{\int^{E_F} E\tilde{D}_{\sigma}(E)dE + \int_{E_F}^{E_F+\delta E_F} E\tilde{D}_{\sigma}(E)dE - \int^{E_F} ED_{\sigma}(E)dE - n_{a\sigma}\varepsilon_{a\sigma}\} \\
&= \sum_{\sigma}\{\int^{E_F} E\Delta D_{\sigma}(E)dE + E_F\tilde{D}_{\sigma}(E_F)\delta E_F - n_{a\sigma}\varepsilon_{a\sigma}\}
\end{aligned}$$

Now using the charge neutrality condition,

$$\int^{E_F+\delta E_F} \tilde{D}_{\sigma}(E)dE - \int^{E_F} D_{\sigma}(E)dE = n_{a\sigma}$$

or

$$\int^{E_F} \Delta D_{\sigma}(E)dE + \tilde{D}_{\sigma}(E_F)\delta E_F = n_{a\sigma}$$

we get,

$$\begin{aligned}
\Delta E(\delta m) &= \sum_{\sigma}\int^{E_F} E\Delta D_{\sigma}(E)dE - E_F\int^{E_F} \Delta D_{\sigma}(E)dE + \sum_{\sigma} E_F(n_{a\sigma} - \varepsilon_{a\sigma}) \\
&= \sum_{\sigma}\int^{E_F} E\Delta D_{\sigma}(E)dE - E_F\int^{E_F} \Delta D_{\uparrow}(E)dE - E_F\int^{E_F} \Delta D_{\downarrow}(E)dE \\
&+ \sum_{\sigma} E_F(n_{a\sigma} - \varepsilon_{a\sigma})
\end{aligned}$$

Now by adding and subtracting $E_F\int^{E_F} \Delta D_{\uparrow}(E)dE$ to right hand side of the above equation we get the Eq.3 of the manuscript.

Calculation of the Stoner parameter for the Fe-(110) film

We have have performed the fixed spin moment calculations for the Fe (110) film. The total energy of the film can be written as,

$$E(m) = E(0) + \frac{1}{2}\chi^{-1}m^2 + \frac{1}{4}\beta m^4 \tag{1}$$

Where E_0 corresponds to the contributions from the non-magnetic degrees of freedoms, χ is the Stoner enhancement of the susceptibility. Therefore, $\chi^{-1} = \frac{\partial^2 E(m)}{dE^2}$. The Stoner parameter is obtained from the from the following [1]

$$I = \frac{1}{N(E_F)} - \frac{2}{\chi} \tag{2}$$

We calculate χ by fitting the Eq.1 to the total energy as shown in the Fig.S1. The calculated value is 0.26.

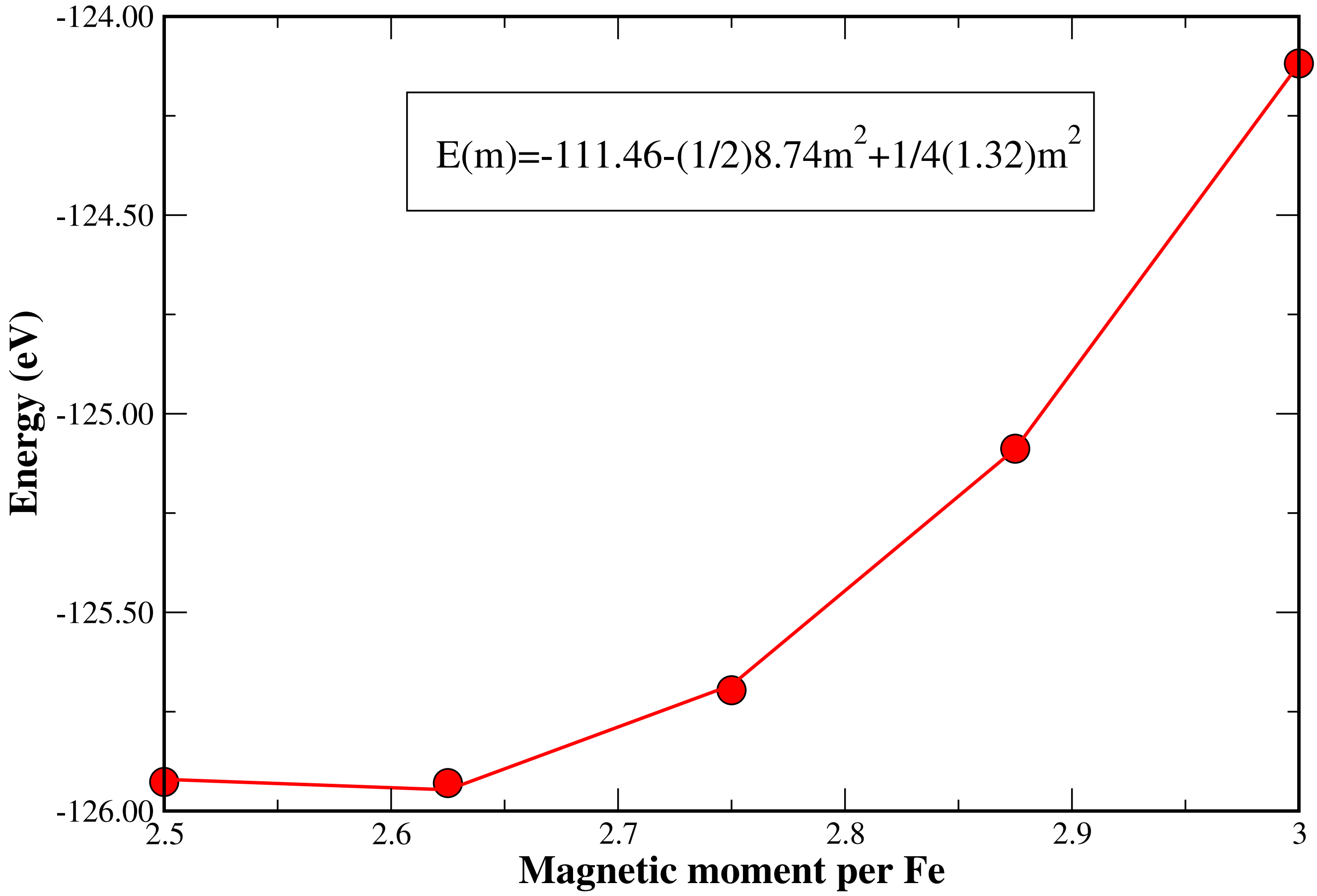

FIG. S1: (Color online) Fixed spin moment energy of bcc (110) surface as a function of the magnetic moment per Fe-atom

Derivation of the Eq.9 of the manuscript

The unperturbed Hamiltonian of the system is given by,

$$H_0 = \sum_{k\sigma} \varepsilon_{k\sigma} c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_{\sigma} \varepsilon_{a\sigma} n_{a\sigma} \tag{3}$$

Where the first term represents the metal Hamiltonian, while the second term is that of the adsorbate. The band index is omitted. The Green's function of the the unperturbed system is given by,

$$G^0_\sigma = \frac{1}{E - H_0 + i\delta} \tag{4}$$

When we switch on the coupling between the two subsytems, the total Hamiltonian becomes,

$$H = H_0 + V \sum_{k,j,\sigma} c^{\dagger}_{k\sigma} c_{a\sigma} + h.c \tag{5}$$

The Green's function for the composite system is given by,

$$G_\sigma = \frac{1}{E - H + i\delta} \tag{6}$$

For each spin, the change in density of states of the metal surface is given by,

$$\Delta D_\sigma(E) = \Delta n_\sigma(E) + \sum_\sigma \delta(\varepsilon - \varepsilon_{a\sigma}) \tag{7}$$

Where,

$$\begin{aligned} \Delta n_\sigma(E) &= -\frac{1}{\pi} Im \left(G_\sigma(E) - G^0_\sigma(E) \right) \\ &= -\frac{1}{\pi} Im \left(\frac{d}{dE} lndet(1 - V G^0_\sigma) \right) \\ &= -\frac{1}{\pi} Im \frac{d}{dE} ln(1 - V^2 \sum_k G^0_{k\sigma} G^0_{a\sigma}) \end{aligned} \tag{8}$$

Where

$$G^0_{k\sigma} = \frac{1}{E - \varepsilon_{k\sigma} + i\delta}$$

and

$$G^0_{a\sigma} = \frac{1}{E - \varepsilon_{a\sigma} + i\delta}$$

are free metal and adsorbate Green's function respectively Therefore from Eq.8

$$\begin{aligned}
\Delta n_\sigma(E) &= -\frac{1}{\pi} Im \frac{d}{dE} ln(1 - V^2 \sum_k \frac{1}{E - \varepsilon_{k\sigma} + i\delta} \frac{1}{E - \varepsilon_{a\sigma} + i\delta}) \\
&= -\frac{1}{\pi} Im \frac{d}{dE} ln(1 - \frac{\Sigma_\sigma(E)}{E - \varepsilon_{a\sigma} + i\delta}) \\
&= -\frac{1}{\pi} Im \frac{d}{dE} \left[ln(E - \varepsilon_{a\sigma} - \Sigma_\sigma(E) - ln(E - \varepsilon_{a\sigma} + i\delta) \right]
\end{aligned} \tag{9}$$

Using the identity below,

$$\frac{d}{dx} lnu(x) = \frac{u'(x)}{u(x)}$$

we get

$$\Delta n_\sigma(E) = -\frac{1}{\pi} Im \left[\frac{(1 - \frac{d\Sigma_\sigma(E)}{dE})}{E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)} \right] - \delta(E - \varepsilon_{a\sigma})$$

after rearranging we get,

$$\begin{aligned}
\Delta n_\sigma(E) + \delta(E - \varepsilon_{a\sigma}) &= -\frac{1}{\pi} Im \left[\frac{(1 - \frac{d\Sigma_\sigma(E)}{dE})}{E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)} \right] \\
\Delta D_\sigma(E) &= -\frac{1}{\pi} Im \left[\frac{(1 - \frac{d\Sigma_\sigma(E)}{dE})}{E - \varepsilon_{a\sigma} - \Sigma_\sigma(E)} \right] \\
&= -\frac{1}{\pi} Im \left[(1 - \frac{d\Sigma_\sigma(E)}{dE}) G_{a\sigma}(E) \right]
\end{aligned} \tag{10}$$

The above equation gives the change in DOS of the adsorbent for a spin σ due to chemisorption. This is used in the manuscript to obtain the most important physical parameters such as adsorption energy, change in surface magnetic moments etc.

[1] L. Ortenzi, I. I. Mazin, P. Blaha, and L. Boeri, Phys. Rev. B **86**, 064437